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12. ABSTRACT (Maximum 200 words) Abstract: The characteristic reactivity of the radical anion OCC ⁻ has been investigated in the gas phase at 298 K through determination of rate coefficients, products, and branching fractions for each of 29 ion-molecule reactions. A wide variety of reactions is observed including abstraction of H, H ⁺ , and H ₂ ⁺ , nucleophilic displacement, charge transfer, and reactions involving electron detachment. Many of the reactions involve cleavage of the C-CO bond, consistent with the relatively small C-CO bond energy and the proposed ¹ electronic structure of the ground state anion in which both radical and charge are centered on the terminal carbon. Similarities are noted between the chemistry of OCC ⁻ and its neutral analogue OCC and between the chemistry of OCC ⁻ and the radical anions O ⁻ and o-C ₆ H ₄ ⁻ . Most reaction products observed are consistent with reaction mechanisms involving initial attack of the terminal carbon in OCC ⁻ on the neutral reaction partner. The gas-phase acidity of HCCO is bracketed between those of CH ₃ NO ₂ and CH ₃ CHO, yielding 1502 ± 8 > ΔG ^o _{acid} (HCCO) ≥ 1463 ± 8 kJ mol ⁻¹ and 1531 ± 12 > ΔH ^o _{acid} (HCCO) ≥ 1491 ± 12 kJ mol ⁻¹ . Observation of H atom transfer from CH ₂ Cl ₂ to OCC ⁻ indicates that ΔH ^o _f (OCC ⁻) ≥ 148 ± 12 kJ mol ⁻¹ and gives a larger lower limit of ΔH ^o _{acid} ≥ 1507 ± 15 kJ mol ⁻¹ . These and related thermochemical values, including the hydrogen bond dissociation energy in HCCO, are compared with literature values.			
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Reactivity of the Radical Anion OCC^- Jane M. Van Doren,^{*,†} Thomas M. Miller,^{‡,‡} Amy E. Stevens Miller,^{‡,§} A. A. Viggiano,[‡]
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Abstract: The characteristic reactivity of the radical anion OCC^- has been investigated in the gas phase at 298 K through determination of rate coefficients, products, and branching fractions for each of 29 ion-molecule reactions. A wide variety of reactions is observed including abstraction of H, H^+ , and H_2^+ , nucleophilic displacement, charge transfer, and reactions involving electron detachment. Many of the reactions involve cleavage of the C-CO bond, consistent with the relatively small C-CO bond energy and the proposed¹ electronic structure of the ground state anion in which both radical and charge are centered on the terminal carbon. Similarities are noted between the chemistry of OCC^- and its neutral analogue OCC and between the chemistry of OCC^- and the radical anions O^- and $\text{o-C}_6\text{H}_5^-$. Most reaction products observed are consistent with reaction mechanisms involving initial attack of the terminal carbon in OCC^- on the neutral reaction partner. The gas-phase acidity of HCCO is bracketed between those of CH_3NO_2 and CH_3CHO , yielding $1502 \pm 8 > \Delta G^\circ_{\text{acid}}(\text{HCCO}) \geq 1463 \pm 8 \text{ kJ mol}^{-1}$ and $1531 \pm 12 > \Delta H^\circ_{\text{acid}}(\text{HCCO}) \geq 1491 \pm 12 \text{ kJ mol}^{-1}$. Observation of H atom transfer from CH_2Cl_2 to OCC^- indicates that $\Delta H^\circ_f(\text{OCC}^-) \geq 148 \pm 12 \text{ kJ mol}^{-1}$ and gives a larger lower limit of $\Delta H^\circ_{\text{acid}} \geq 1507 \pm 15 \text{ kJ mol}^{-1}$. These and related thermochemical values, including the hydrogen bond dissociation energy in HCCO, are compared with literature values.

Introduction

OCC^- is a radical anion which, we will show, has a rich chemistry. The photoelectron spectrum, investigated by Oakes et al.,¹ gives insight as to the electronic structure of OCC^- . On the basis of their data and general valence bond considerations, the investigators assigned the ground state of OCC^- to $^2\Pi$ with the charge and radical centered on the terminal carbon. The distonic configuration, with the charge centered on the oxygen and the radical centered on the terminal carbon, is not the same symmetry—it is $^2\Sigma^+$ —and does not contribute to the $^2\Pi$ state. Using the electron affinity of OCC found by Oakes et al.¹ and other thermochemical data in the literature,^{2,3} we can determine that the C-CO bond is the weakest in the molecule. We will see, in the reactivity studies discussed below, that the observed reactions are consistent with the $^2\Pi$ state assignment and that the location of the charge and small C-CO bond energy play a large role in the reactivity of this anion. In particular, many of the reactions appear to proceed with initial bonding of the terminal carbon to the neutral reactant, accompanied by cleavage of the C-CO bond. As a result of these characteristics as well as its radical nature, we find that this anion can participate in a wide variety of reactions.

Observations of ions in flames have not identified OCC^- , but our previous work on the reactivity of the dicarbon anion⁴ indicates that OCC^- is formed in most if not all hydrocarbon-oxygen flames. In particular, the dicarbon anion, C_2^- , which is a dominant negative

ion in combustion plasma,⁵ reacts efficiently with oxygen to form OCC^- . In addition, OCC^- may be formed from other species in the plasma, such as from OCC and HCCO, which are known intermediates in the oxidation of hydrocarbons. Perhaps more important, however, is the direct role of these neutral relatives in hydrocarbon oxidations. For example, the oxidation of acetylene to carbon monoxide is believed to proceed principally through three oxidation steps involving the formation of HCCO and OCC (see, for example, the work of Bayes and co-workers⁶⁻⁸). The oxidation of acetylene and other hydrocarbon oxidation reactions have been studied by a variety of techniques, yet questions about the mechanism, reactions, and thermochemistry involved still remain. One such uncertainty concerns the hydrogen atom bond energy in HCCO, which is important for accurate modeling of combustion processes.⁹ In this study, we evaluate the acidity of HCCO, which, taken together with the electron affinity of OCC and the ionization potential of hydrogen, lead to a determination of this bond energy. Our data lead to values for the heats of formation of OCC and OCC^- and therefore the bond energies in OCC^- .

Interest in the neutral OCC as a reaction intermediate in hydrocarbon oxidations,^{6-8,10,11} as well as in photolysis of carbon suboxide,¹²⁻¹⁴ oxidation of carbon suboxide,⁶ and pulse radiolysis of CO,¹⁵ has led to detailed studies of its chemical reactions. In many of its reactions, this molecular species reacts by carbon atom transfer with loss of CO. For example, reaction with olefins¹³

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proceeds by insertion of the carbon atom into the multiple bond, leading to formation of an allene. The similar reactivity of OCC and the C atom, which leads to identical products in many cases, makes it difficult to determine the role of the individual species in systems where both species are expected to be present.¹⁶ As mentioned above, OCC⁻ also has a propensity to break the carbon-carbon bond and to donate, in this case, a C⁻ ion. However, OCC⁻ is not expected to react in a fashion similar to C⁻ because these two ions have such different electronic structures, i.e., both differing symmetry and spin, whereas the analogous neutral species have the same ground state electronic designation. In addition, we note that OCC⁻ does not correlate with ground state dissociation products C⁻ + CO, that is to say, it cannot be expected to react like the ground state solvated species C⁻(CO). The anion OCC⁻ does correlate to the higher energy products C⁻ + CO (³Π). However, dissociation of OCC⁻ to these products requires an additional¹⁷ 580 kJ mol⁻¹ over the ground state bond dissociation energy, indicating that reactions forming CO (³Π) will generally be endothermic and therefore will not be observed in our room temperature experiment. OCC⁻ may be expected to react in a similar fashion to O⁻ which is also a radical anion with the same symmetry. We find that many of the reactions characteristic of O⁻ also occur with OCC⁻, for example, H₂⁺ abstraction.

Experimental Section

The reported measurements were made with a selected ion flow drift tube which has been described in detail previously.^{18,19} The reactant OCC⁻ was formed from carbon suboxide in a remote high-pressure (~0.1–1 Torr) ion source, presumably by dissociative electron attachment. The carbon suboxide was synthesized by dehydration of malonic acid with phosphorus pentoxide as described by Long et al.²⁰ The OCC⁻ ions were mass selected and injected into the reaction flow tube. These ions were carried through the flow tube by a laminar flow of helium. The ions were allowed to react with neutral species which were injected through one of two inlets. At the end of the flow tube, the gas flow was sampled through a 0.2 mm sampling orifice located in the center of the sampling plate which was electrically isolated from the vacuum housing and connected to an electrometer. The ions sampled were mass analyzed and counted with a particle multiplier.

A rate coefficient was determined from the decrease in reactant ion count rate with increasing neutral flow through a single inlet. This attenuation was measured for two neutral inlet positions to determine the end correction, or the effective neutral mixing distance. The reported rate coefficients are an average of at least four measurements (2 at each inlet). Relative error is estimated to be ±15%, while absolute error is estimated to be ±25%.¹⁹

Branching percentages were determined by monitoring the product ion signals as a function of reactant neutral flow rate. A particular product branching fraction was evaluated from a plot of the signal for the product ion divided by the total signal for all ionic products versus reactant neutral flow rate. The curve formed was extrapolated to zero flow, and this value is reported, after being converted to a percentage. In reactions forming products containing chlorine atoms, the measured percentages were further corrected for the natural isotopic abundance since only the major chlorine isotope was monitored. In those reactions of OCC⁻ where a loss in total ion signal at the particle multiplier was observed upon addition of the neutral reactant, the presence of at least one reactive channel involving electron detachment was indicated. This interpretation was confirmed and quantified by observation of a loss of current to the sampling plate, since electrons formed in the flow tube are inefficiently detected in our apparatus^{21,22} due to the large diffusional loss of these species to the flow tube wall. For these reactions, branching percentages for individual ionic products were determined as above and multiplied by the branching fraction for all ionic products. The branching between ionic products

and electron detachment products was evaluated from a comparison of the initial sampling plate current to the final current at reaction completion.²³ The branching fractions were approximate; ionic product signals were not corrected for detection discrimination, although the detection conditions were set so as to minimize mass discrimination, and both ionic and electron detachment branching fractions neglect differential diffusion. Precision of branching fractions was typically ±5%. Assuming that differences in detection sensitivities and diffusion coefficients are small, we estimate that the reported branching fractions are accurate to ±10 percentage points for major (>10%) ionic products relative to other ionic products, ±20 percentage points for electron detachment products, and a factor of 0.5 of the branching fraction value for minor (<10%) products.

The neutral reagents were from sources and of purities as follows: C(O)F₂ (carbonyl fluoride, PCR 97% min), CS₂ (Baker, 99%), COS (Matheson, 97.5%), CO₂ (Matheson, 99.8%), O₂ (Matheson, 99.997%), CO (Matheson, 99.99%), H₂S (Matheson, 99.5%), CH₃F (Matheson, 99%), CH₃Cl (Matheson, 99.5%), CH₃Br (Matheson, 99.5%), CH₂Cl₂ (Aldrich, 99.9%), CHCl₃ (J. T. Baker Co., 99.8% min), CH₃NO₂ (Aldrich, 99+%), CF₃CH₂OH (Aldrich, 99.5+%), CH₃CH₂OH (U. S. I., 99.9%), CH₃CHO (acetaldehyde, Kodak, 99%), CH₃C(O)CH₃ (acetone, Aldrich, 99+%), C₂H₂ (Matheson, 99.6%), CF₃CCH (PCR, 97%), CH₃CCH (Linde Specialty Gas, 96.0%), C₇H₈ (toluene, Aldrich, 99+%), C₂H₄ (Scientific Gas Products, 99.5%), NO (Matheson, 99.0% min with lot impurities of 0.25% N₂O and <0.5% NO₂; in separate experiments we set a limit on the NO₂ impurity in the NO of ≤0.8%), SO₂ (Scientific Gas Products, 99.98%), HF (Matheson, 99.9%), N₂O (Scientific Gas Products, CP grade), H₂ (Matheson, 99.99%), N₂ (Matheson, 99.999%). These reagents were used without further purification, except that all liquid reagents were subject to ≥2 freeze-pump-thaw cycles.

The rate coefficient and branching percentage measurements of the reactions of OCC⁻ with nitrogen dioxide were made with a mixture of ~1% NO₂ in helium at 1 atm to minimize the amount of NO₂ dimers entering the flow tube. We estimate that <2% dimers are present in this mixture, using the equilibrium constant value of 0.81 (K_p) for the dimerization reaction at 298 K.²⁴ Samples were either prepared in the laboratory with neat NO₂ (Matheson, 99.5%) and high purity helium (99.997%) or taken from a 1% mixture of NO₂ in He provided by Matheson with the same nominal purity levels.

Results and Discussion

We have investigated the reaction of OCC⁻ with a variety of neutral molecules. The rate coefficients and branching percentages at 298 K are presented in Table I. Ionic products were experimentally identified only by mass, and neutral products were inferred from mass balance and known thermochemistry. Brief perusal of the table shows that OCC⁻ often reacts to form an ionic product plus CO or CO₂. Abstraction of a hydrogen atom or an H₂⁺ from neutral reaction partners as well as OCC⁻ acting as a nucleophile in displacement reactions is also observed. In addition, OCC⁻ reacts with many organic species by proton abstraction, if it is exothermic to do so, and by reactive electron detachment (RD), producing a free electron and one or more neutral products. (As defined, RD includes associative detachment, detachment reactions which involve molecular rearrangement including bond formation and dissociation, and collisional detachment reactions.) Most reaction products observed are consistent with reaction mechanisms involving initial attack of the terminal carbon in OCC⁻ on the neutral reaction partner. A detailed discussion of many of these reactions follows.

In several reactions, OCC⁻ transfers a C⁻ (presumably the terminal carbon) to the reactant neutral, leaving a CO neutral product. For example, in the reaction with carbonyl fluoride, C₂F₂O⁻ is formed.



The product ion formed is likely a distonic ion, either the initially formed structure shown above or possibly CF=CF⁻O⁻ arising from intramolecular F atom transfer from CCF₂O⁻. The anion

(16) Peterson, R. F., Jr.; Wolfgang, R. L. *Chem. Commun.* 1968, 20, 1201.

(17) Huber, K. P.; Herzberg, G. *Constants of Diatomic Molecules*; Van Nostrand: Reinhold, NY, 1979.

(18) Viggiano, A. A.; Morris, R. A.; Paulson, J. F. *J. Chem. Phys.* 1989, 90, 6811.

(19) Viggiano, A. A.; Morris, R. A.; Dale, F.; Paulson, J. F.; Giles, K.; Smith, D.; Su, T. *J. Chem. Phys.* 1990, 93, 1149.

(20) Long, D. A.; Murfin, F. S.; Williams, R. L. *Proc. R. Soc. London, Ser. A* 1954, 223, 17.

(21) Viggiano, A. A.; Paulson, J. F. *J. Chem. Phys.* 1983, 79, 2241.

(22) Morris, R. A. *J. Chem. Phys.* 1992, 97, 2372.

(23) Viggiano, A. A.; Morris, R. A.; Paulson, J. F.; Ferguson, E. E. *J. Phys. Chem.* 1990, 94, 7111.

(24) Atkins, P. W. *Physical Chemistry*; W. H. Freeman and Co.: San Francisco, 1978; p 254.

Table I. Reaction Products and Rate Coefficient Values at 298 K for Reaction of OCC⁻ with Neutral Reactant Indicated

neutral reactant	products ^a	branching percentage ^b	rate coefficient ^c (10 ⁻¹⁰ cm ³ s ⁻¹)	efficiency ^d
C(O)F ₂	C ₂ F ₂ O ⁻ + CO	100	9.7	0.85
CS ₂	C ₂ S ₂ ⁻ + CO	6	9.7	0.72
	C ₂ OS ⁻ + CS	94		
COS	C ₂ OS ⁻ + CO	100	4.4	0.32
CO ₂ + He	C ₃ O ₃ ⁻	100	0.026 at 0.4 torr <i>k</i> (III) = 2.0 (-28) ^e	0.3% at 0.4 Torr
O ₂	RD(CO ₂ + CO + e)	65	1.1	0.16
	O ⁻ + 2CO	35		
CO	RD(C ₃ O ₂ + e)	100	0.33	0.04
H ₂ S	RD(C ₂ H ₂ SO + e)	39	21	1.35 ^f
	S ⁻ + H ₂ C ₂ O	24		
	HC ₂ O ⁻ + HS	21		
	HS ⁻ + HC ₂ O	16		
CH ₃ F	NR ^g		<i>h</i>	
CH ₃ Cl	NR ^g		<0.04	<0.002
CH ₃ Br	Br + CH ₃ C ₂ O	100	2.1	0.10
CH ₂ Cl ₂	CCl ₂ ⁻ + H ₂ C ₂ O	49	1.5	0.08
	Cl ⁻ + CH ₂ ClC ₂ O	32		
	HC ₂ O ⁻ + CHCl ₂	19		
CHCl ₃	Cl ⁻ + CHCl ₂ C ₂ O	78	8.5	0.52
	CCl ₃ ⁻ + HC ₂ O	22		
CH ₃ NO ₂	CH ₂ NO ₂ ⁻ + HC ₂ O	5	16	0.43
	NO ₂ ⁻ + CH ₃ C ₂ O	93		
	<i>m/e</i> 71 + neutral	2		
CF ₃ CH ₂ OH	RD	major	26 ⁱ	<i>j</i>
	CF ₃ CH ₂ O ⁻ + HC ₂ O	minor		
CH ₃ CH ₂ OH	RD	major	2.6	0.12
CH ₃ CHO	RD	major	2.9	0.09
CH ₃ C(O)CH ₃	RD	major	1.8	0.06
HCCCH	NR ^g		<0.065	<0.006
CF ₃ CCH	CF ₃ CC ⁻ + HC ₂ O	major	6 ⁱ	<i>j</i>
CH ₃ CCH	NR		<0.03	<0.002
C ₇ H ₈ (toluene)	NR ^k		<0.2	<0.01
C ₂ H ₄	NR		<0.01	<0.0009
NO	CNO ⁻ + CO	96	2.2	0.28
	CN ⁻ + CO ₂	4		
NO ₂	RD(2CO + NO + e)	55	10	1.0
	CNO ⁻ + CO ₂	28		
	CN ⁻ + CO ₂ + O	9		
	NO ₂ ⁻ + OCC	8		
SO ₂	OCS ⁻ + CO ₂ ^l	100	1.0	0.55
HF	NR ^g		<0.3	<0.01
N ₂ O	NR		<0.009	<0.001
H ₂	NR		<0.01	<0.0007
N ₂	NR ^g		<0.006	<0.0008

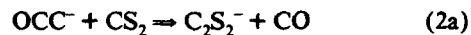
^a Ionic products are observed. Neutral products are inferred from mass balance. RD indicates a reactive electron detachment channel as indicated by total signal loss or decrease in sampling plate current (see text). NR indicates no observable decay of the reactant ion signal intensity and no product ions detected. ^b Precision of branching fractions was typically $\pm 5\%$. Assuming that different detection sensitivities and diffusion coefficients are small, we estimate that the reported branching fractions are accurate to ± 10 percentage points for major ($>10\%$) ionic products relative to other ionic products, ± 20 percentage points for RD products, and a factor of 0.5 of the branching fraction value for minor ($<10\%$) products. ^c Total reaction rate coefficient. Uncertainty is estimated to be $\pm 25\%$ absolute, $\pm 15\%$ relative. ^d Efficiency is the ratio of the measured rate coefficient to the calculated collision rate coefficient. Collision rate coefficients were calculated using the parametrized trajectory theory developed by Su and Chesnavich.^{64,65} ^e *k*(III) is the third order rate coefficient with units of cm⁶ s⁻¹ noting that $2.0(-28) = 2.0 \times 10^{-28}$. ^f Efficiencies greater than 1 reflect uncertainties in the calculated collision rate coefficient and measured reaction rate coefficient. ^g Some ionic products or loss in overall ion signal was observed but is suspected to arise from impurities in the neutral reagent sample/flow. Reaction of indicated neutral with OCC⁻ is at most slow, as indicated by the rate coefficient limit given. ^h No rate coefficient limit was determined. ⁱ Unable to estimate collision rate coefficient. ^j Uncertainty is estimated to be $\pm 40\%$ absolute, $\pm 25\%$ relative. ^k Neutral flow rate was limited by vapor pressure. For flows introduced, no loss in primary ion signal or production of ionic products was observed. Reaction is at most inefficient. ^l See text for discussion.

O⁻, a radical anion of the same symmetry as OCC⁻, ²II, also reacts with C(O)F₂. A distonic configuration has been proposed as an intermediate in the reaction of O⁻ with C(O)F₂.^{25,26} In contrast with OCC⁻, however, the distonic association product ion CO₂F₂⁻ from reaction of C(O)F₂ with O⁻ is not observed but goes on to lose an F atom forming CO₂F⁻. Possibly the CO lost in the reaction with OCC⁻ (eq 1) carries off enough excess energy so as to preclude further decomposition of the C₂F₂O⁻ ion. Alternatively, the C-C bond formed is not sufficiently strong to thermochemically allow further decomposition of the ion.

(25) Dawson, J. H. J.; Noest, A. J.; Nibbering, N. M. M. *Int. J. Mass Spectrom. Ion Phys.* 1979, 29, 205.

(26) Lee, J.; Grabowski, J. J. *Chem. Rev.* 1992, 92, 1611-1647 and references therein.

Transfer of C⁻ also occurs in reaction of OCC⁻ with CS₂, reaction 2a,



but the product arising from sulfur atom transfer to the reactant ion dominates, reaction 2b. Formation of C₂S₂⁻ may proceed by attack of the terminal carbon of OCC⁻ on the carbon atom in CS₂, while formation of C₂OS⁻ arises from its attack on one of the sulfur atoms.

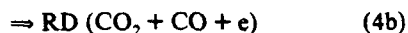
Reaction of OCC⁻ with COS by either C⁻ transfer to COS or S transfer to OCC⁻ results in the same product ion, C₂OS⁻, which is the observed product ion.



Previous studies have shown that COS and CS₂ react in a similar fashion with a variety of ions (see, for example, work of DePuy and co-workers²⁷⁻³⁰). Therefore, by analogy with CS₂, we expect that most, if not all, of reaction 3 proceeds by sulfur atom transfer to OCC⁻. Isotopic labeling of the oxygen or carbon atoms in the reactants is needed in future work, since products of such a reaction would determine the reaction mechanisms involved.

Reaction of OCC⁻ with CO₂ is slow, forming only the association product C₃O₃⁻. The ionic product analogous to the products observed in reactions 2 and 3 would be C₂O₂⁻ and is not observed. Although the anion C₂O₂⁻ is not likely to be stable, observation of a loss in signal denoting a reactive electron detachment channel arising from loss of an electron from the temporary negative ion formed (forming in the overall reaction 3CO + e) would suggest that the C⁻ and/or O atom transfer pathways were occurring. However, no reactive electron detachment channel is observed in reaction with CO₂. In contrast, reaction of the isolated C⁻ with CO₂ apparently does form 2CO + e.³¹ The rate coefficients observed for the series CS₂, COS, and CO₂ indicate that reaction efficiency decreases with increasing oxygen substitution.

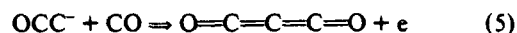
Reaction of OCC⁻ with oxygen also appears to form CO as a product and includes a reactive electron detachment channel (RD) as well.



While the reactive electron detachment products could also be O + 2CO + e, arising from loss of an electron from the O⁻ product ion before separation of the products (due to the large exothermicity of the reaction), we suggest they are CO₂ + CO + e based on related reactions reported in the literature. In particular, in the reaction³¹ of C⁻ with O₂, which also forms O⁻ + CO with enough energy to detach an electron from the product O⁻, little or no reactive electron detachment is observed. In addition, the suggested products CO₂ + CO + e for the observed reactive electron detachment channel 4b are supported by the work of Peterson and Wolfgang.¹⁶ They investigated the related neutral reaction of OCC + O₂ which forms O + 2CO and CO₂ + CO, product channels which appear to be analogous to those in eqs 4a and 4b. Using isotopically labeled reactants they found that the terminal carbon in OCC is not incorporated into the CO₂ neutral. These results led them to suggest that the reaction proceeds through a four-center transition state between the oxygens and carbons which is a precursor to both reaction channels. A similar reaction mechanism could be operating in ion-molecule reaction 4. One can also imagine that reaction 4 proceeds stepwise, forming the products in eq 4a first, from attack of the terminal carbon in OCC⁻ on one of the oxygens, followed by intracomplex associative detachment of O⁻ with one of the CO molecules forming CO₂ + CO + e, the products in reaction 4b. The associative detachment reaction of O⁻ with CO is efficient at 298 K.³²⁻³⁵ The absence of a significant reactive electron detachment channel in the reaction³² of C⁻ with O₂ which also produces O⁻

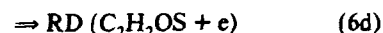
+ CO and cannot react *via* a four-center transition state, however, would suggest that this mechanism is less likely.

Reaction of OCC⁻ with CO results only in reactive electron detachment. The neutral product must be the associative detachment product carbon suboxide, based on energetic considerations, and presumably arises from bonding of the terminal carbon in the anion to the carbon in CO.



Formation of carbon suboxide in reaction 5 is the reverse of the reaction used to form OCC⁻ in the ion source of our apparatus. (Reactivity of carbon suboxide with anions has been investigated and summarized in a study by Roberts and DePuy.³⁶) Simple transfer of C⁻ (with concomitant loss of CO) from OCC⁻ to CO may occur but cannot be detected in our experiments as it is a symmetric exchange reaction.

A variety of reaction products is observed in the reaction of OCC⁻ with H₂S.



The species H₂⁺, H, and H⁺ are transferred in reactions 6a-c, respectively. We assign the reactive electron detachment channel 6d to associative detachment because all other detachment channels are endothermic. Although proton abstraction often dominates when exothermic, H atom abstraction can occur as a result of electron transfer from the proton abstraction products, as the products separate. For example, in reaction 6 proton abstraction forms HS⁻ + HCCO. The electron affinities of HCCO and HS are almost the same, differing by less than 0.1 eV. Therefore, one expects some electron transfer from HS⁻ to HCCO as the products separate, forming the "H atom abstraction" products, and this channel is observed. Indeed, in the reactions of O⁻ with substituted methanes, Melly and Grabowski³⁷ report H atom abstraction in competition with proton abstraction in all reactions where H atom abstraction was more exothermic; the difference in exothermicity of H⁺ and H abstraction is simply the difference in the neutral product electron affinities. Transfer of an H₂⁺ to the anion forms the ketene neutral, reaction 6a. Such a reaction has been observed in reactions^{26,38} of the O⁻ and benzyne radical anions and, in the case of O⁻, has been exploited to form a variety of novel carbene radical anions.²⁶ Preliminary investigation of the reaction of O⁻ with H₂S by Grabowski and co-workers³⁹ indicates that H₂⁺ and proton abstraction channels proceed. In contrast with the OCC⁻ reaction, however, proton abstraction dominates in the O⁻ reaction (~6:1), a consequence of the greater basicity of this anion.³⁹ The observation and efficiency of H₂⁺ abstraction in reaction of OCC⁻ with H₂S suggests that reactions of OCC⁻ with other organic hydrides may lead to the formation of new anionic carbenes *via* the H₂⁺ abstraction reaction since OCC⁻ accesses a reactivity regime different from that of O⁻ due to its weaker basicity. However, the fact that formation of ketene in reactions of OCC⁻ is not as large an energetic driving force as formation of H₂O in analogous reactions of O⁻ indicates that the range of species for which H₂⁺ abstraction is energetically accessible is smaller for OCC⁻ than for O⁻.

Reaction of OCC⁻ with halogenated methanes proceeds by a number of different reaction pathways, including nucleophilic

(27) Bierbaum, V. M.; Grabowski, J. J.; DePuy, C. H. *J. Phys. Chem.* 1984, 88, 1389-1393.

(28) DePuy, C. H. In *Ionic Processes in the Gas Phase*; Ferreira, M. A., Ed.; D. Reidel Publishing Co.: New York, 1984; pp 227-241.

(29) DePuy, C. H. *Org. Mass Spectrom.* 1985, 20, 556.

(30) DePuy, C. H.; Van Doren, J. M.; Gronert, S.; Kass, S. R.; Motell, E. L.; Ellison, G. B.; Bierbaum, V. M. *J. Org. Chem.* 1989, 54, 1846.

(31) Fehsenfeld, F. C.; Ferguson, E. E. *J. Chem. Phys.* 1970, 53, 2614.

(32) Parkes, D. A. *J. Chem. Soc., Faraday Trans. 1* 1972, 68, 613.

(33) McFarland, M.; Albritton, D. L.; Fehsenfeld, F. C.; Ferguson, E. E.; Schmeltekopf, A. L. *J. Chem. Phys.* 1973, 59, 6629.

(34) Viggiano, A. A.; Morris, R. A.; Deakne, C. A.; Dale, F.; Paulson, J. F. *J. Phys. Chem.* 1990, 94, 8193.

(35) Van Doren, J. M.; Barlow, S. E.; DePuy, C. H.; Bierbaum, V. M. *Int. J. Mass Spectrom. Ion Proc.* 1991, 109, 305.

(36) Roberts, C. R.; DePuy, C. H. *J. Gen. Chem., USSR (Engl. Transl.)* 1989, 59, 1931.

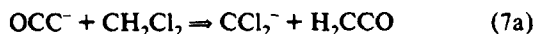
(37) Grabowski, J. J.; Melly, S. J. *Int. J. Mass Spectrom. Ion Proc.* 1987, 81, 147.

(38) Guo, Y.; Grabowski, J. J. *J. Am. Chem. Soc.* 1991, 113, 5923.

(39) Grabowski, J. J., personal communication, 1992.

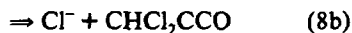
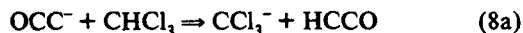
displacement ($\text{S}_{\text{N}}2$) and abstraction of H^+ , H , and H_2^+ . Little or no reaction occurs with CH_3F and CH_3Cl , while reaction with CH_3Br proceeds with modest efficiency to form Br^- . Greater $\text{S}_{\text{N}}2$ reaction efficiency for reaction with CH_3Br as compared with CH_3Cl or CH_3F , as observed for OCC^- , is consistent with the behavior of other anions.⁴⁰

Reaction channels other than $\text{S}_{\text{N}}2$ displacement occur when chlorine substitution increases. In reaction with CH_2Cl_2 ,



H_2^+ abstraction forming ketene and CCl_2^- (eq 7a) and H atom abstraction forming HCCO^- (eq 7c) are observed in addition to the $\text{S}_{\text{N}}2$ displacement channel (eq 7b), all proceeding with comparable efficiencies. While we have no direct evidence concerning the identity of neutral products, we believe the product channel forming Cl^- , reaction 7b, is an $\text{S}_{\text{N}}2$ reaction forming the CH_2ClCCO neutral rather than a dissociative electron transfer reaction because the latter reaction is highly endothermic. Of course, we do not know whether the neutral product rearranges. The observation of H atom abstraction, reaction 7c, indicates that the reaction is exothermic or nearly so and places a limit on $\Delta H^\circ_f(\text{OCC}^-)$ of $\geq 148 \pm 12 \text{ kJ mol}^{-1}$ using the literature values for the standard heats of formation of the other species involved.^{1,3} This limit and its implications for the acidity of HCCO and related thermochemical data will be discussed further below in the Acidity and Related Thermochemical Data section. The anion O^- reacts with CH_2Cl_2 in a similar fashion, by H_2^+ abstraction, $\text{S}_{\text{N}}2$ displacement, and H atom abstraction, but in addition by proton abstraction. Benzyne radical anion also reacts with CH_2Cl_2 by H_2^+ and proton abstraction.³⁸ We presume that the absence of proton abstraction in reaction with OCC^- indicates that this reaction is endothermic (see below). The observation of H atom abstraction from a substituted methane when proton abstraction is endothermic is consistent with the trends observed by Melly and Grabowski³⁷ for the reactions of O^- . They found that reaction of O^- with species less acidic than HO proceeded exclusively by H atom abstraction.

Further chlorine substitution increases the acidity of the halogenated methane CHCl_3 as compared with the other halogenated methanes studied and consequently leads to the observation of proton abstraction in reaction with OCC^- . Nucleophilic displacement is also observed. As in reaction 7b, we assume the reaction channel forming Cl^- is a nucleophilic displacement reaction as opposed to a dissociative electron transfer reaction because the latter reaction is highly endothermic. Again, since our experiment does not directly probe neutral products, we cannot know whether the neutral product rearranges.



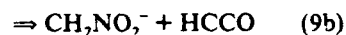
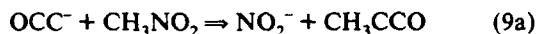
Obviously, CHCl_3 does not have two hydrogen atoms to allow the H_2^+ channel to occur. Hydrogen atom abstraction by OCC^- is not observed. The absence of the H atom abstraction channel is surprising because current values indicate that CCl_3 has a smaller electron affinity ($2.25 \pm 0.1 \text{ eV}^{41}$) than HCCO ($2.35 \pm 0.02 \text{ eV}^{1}$). As discussed above for reaction 6, H atom transfer can occur in two steps, namely proton transfer followed by electron transfer. In reaction 8a, proton transfer forms $\text{CCl}_3^- + \text{HCCO}$. As the products separate, one would expect the electron to transfer to the moiety with the higher electron affinity, in this case HCCO .

(40) Ikezoe, Y.; Matsuo, S.; Takebe, M.; Viggiano, A. A. *Gas Phase Ion-Molecule Reaction Rate Constants Through 1986*; Maruzen Company, Ltd.: Tokyo, 1987, and references therein.

(41) Paulino, J. A.; Squires, R. R. *J. Am. Chem. Soc.* 1991, 113, 5573.

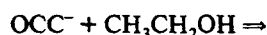
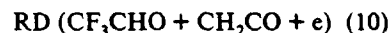
Rapid electron transfer between separating products in low-energy ion-molecule reactions has been implicated in isotopic exchange studies before.⁴³ The absence of this reaction suggests that other reasons, such as poor Franck-Condon overlap for electron detachment of CCl_3^- to form CCl_3 , may prevent H atom abstraction. The rate coefficients measured for the chlorinated methanes indicate that the overall reaction efficiencies increase with increasing Cl substitution, possibly due to the concomitant increasing acidities.

The anion OCC^- displaces NO_2^- from CH_3NO_2 in most of the reactive collisions, reaction 9a. As in reactions 7b and 8b, we designate this reaction as a displacement reaction, forming NO_2^- and the CH_3CCO neutral, because dissociative electron transfer is highly endothermic. Two other product channels are also observed in the reaction of OCC^- with CH_3NO_2 .



Inefficient proton abstraction (reaction 9b) and a reaction channel forming $m/e \text{ 71}$ and a neutral (reaction 9c) occur in a small fraction of the collisions of these species. The products for reaction 9c could be $\text{C}_3\text{H}_3\text{O}_2^- + \text{NO}$ or $\text{C}_2\text{HNO}_2^- + \text{CH}_2\text{O}$, where the former products could arise from an intracomplex reaction of NO_2^- with CH_3CCO . H atom abstraction is not observed despite the fact that estimates for the electron affinity of CH_2NO_2 indicate that charge transfer from CH_2NO_2^- to HCCO is exothermic.^{1,3} While reaction of the radical anion O^- with CH_3NO_2 similarly includes displacement and proton abstraction, H and H_2^+ abstraction are also observed.³⁷ The absence of the H_2^+ product ion in the reaction of OCC^- with CH_3NO_2 may indicate that this channel is energetically inaccessible.

The major reactive pathway for reaction of the radical anion OCC^- with the $\text{CF}_3\text{CH}_2\text{OH}$ and $\text{CH}_3\text{CH}_2\text{OH}$ is reactive electron detachment.



In light of the ability of OCC^- to abstract an H_2^+ , we suggest that these reactions involve H_2^+ transfer to the OCC^- anion with detachment of the electron from the resulting negative ion. The closed shell neutral products formed from such a mechanism are indicated in parentheses for each of the observed reactions. A similar conclusion was reached by Guo and Grabowski³⁸ for reaction of benzyne radical anion with alcohols where they believe the neutral products benzene and the corresponding aldehyde are formed. Robinson et al.⁴² observed extensive signal loss in reaction of the C_3H_2^- radical anion formed in the reaction of O^- with allene (which they believe to be the propadienylidene anion CH_2CC^-) with a variety of alcohols. No H_2^+ abstraction or reactive electron detachment products have been observed in the reaction of O^- with simple aliphatic alcohols, but proton abstraction is exothermic and could preclude such a reaction.²⁶

Similarly, OCC^- reacts with acetaldehyde and acetone by reactive electron detachment.



(42) Robinson, M. S.; Polak, M. L.; Bierbaum, V. M.; DePuy, C. H.; Lineberger, W. C., preliminary results. Extensive signal loss, interpreted as reactive electron detachment, was observed in most reactions of the C_3H_2^- anion formed in the reaction of O^- with allene. The photoelectron spectrum suggests that a single $(M-2)^-$ is formed in the reaction of O^- with allene, in contrast with the results of Grabowski, J. J. In *Advances in Gas Phase Ion Chemistry*; Adams, N. G.; Babcock, L. M., Eds.; JAI Press Inc.: Greenwich, in press, and discussed in Ref. 25.



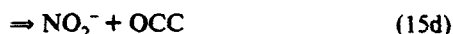
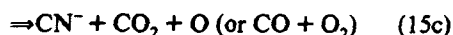
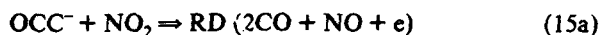
The lack of detectable ionic products in these reactions was initially disturbing in light of limited precedence in the literature for similar reactions. However, there is at least one example in the literature where a major reactive electron detachment reaction channel was observed in reaction of a radical anion with an aldehyde, the reaction of CH_2^- with $\text{CH}_2\text{CHC}(\text{O})\text{H}$,^{43,44} and preliminary data of Robinson et al.⁴² suggest major reactive electron detachment products are formed in several reactions of the C_3H_2^- radical anion (formed in the reaction of O^- with allene) with ketones. Finally, studies of radical anion reactions are limited, and reactive electron detachment channels have been observed in many other ion-molecule reactions.^{4,22,38,42-47} Reaction of O^- with acetaldehyde³⁷ and acetone⁴⁸⁻⁵⁰ proceeds by several pathways including H_2^+ abstraction, forming a stable negative ion in each case. Further investigation of these and other reactions of OCC^- with organic species under conditions of better signal-to-noise would make identification of any minor anionic products possible which could shed light on the operative mechanisms and neutral products involved in the reactive electron detachment reactions.

Two products are observed in the reaction of OCC^- with NO .



The product ion in reaction 14a could be either CNO^- or NCO^- based on available thermochemical data,⁵¹⁻⁵³ but CNO^- seems most reasonable mechanistically as it may be formed by transfer of the terminal carbon in OCC^- followed by cleavage of the weak C-CO bond. In contrast, formation of NCO^- requires insertion of a carbon into the NO bond. The product ions CNO^- and CN^- have been observed in the related reaction of C_2^- with NO_2 and attributed to the formation of $[\text{OCC}^- + \text{NO}]$ in the collision complex.⁴ We note that the ion-molecule literature in general has ignored the isomeric fulminate anion (CNO^-) as a possible product ion in favor of the cyanate ion (NCO^-). We have made preliminary attempts to distinguish these species by their reactions in the gas phase but have been unsuccessful to date. The neutral product in reaction 14b could be either CO_2 or $\text{CO} + \text{O}$, based on energetics alone. If reaction 14b proceeds through a four-center transition state as suggested for the reaction of OCC^- with O_2 , the neutral product is likely to be CO_2 .

Reaction of OCC^- with NO_2 is efficient, forming products upon every collision. Four product channels are observed, with the reactive electron detachment channel dominating.



The anion NO_3^- was also observed but is attributed to reaction

(43) Van Doren, J. M. Ph.D. Thesis, University of Colorado, 1987.

(44) DePuy, C. H.; Barlow, S. E.; Van Doren, J. M.; Roberts, C. R.; Bierbaum, V. M. *J. Am. Chem. Soc.* 1987, 109, 4414.

(45) Viggiano, A. A.; Morris, R. A.; Paulson, J. F. *J. Phys. Chem.* 1990, 94, 3286.

(46) Van Doren, J. M.; Viggiano, A. A.; Morris, R. A.; Stevens Miller, A. E. S.; Miller, T. M. M.; Paulson, J. F.; Deakyne, C. A.; Michels, H. H.; Montgomery, J. A., Jr. *J. Chem. Phys.* 1993, 98, 7940.

(47) Miller, A. E. S.; Miller, T. M.; Morris, R. A.; Viggiano, A. A.; Van Doren, J. M.; Paulson, J. F. *Int. J. Mass Spectrom. Ion Proc.* 1993, 123, 205.

(48) van der Wel, H.; Nibbering, N. M. M. *Recl. Trav. Chim. Pays-Bas* 1988, 107, 479.

(49) Harrison, A. G.; Jennings, K. R. *J. Chem. Soc., Faraday Trans. 1* 1976, 72, 1601.

(50) Dawson, J. H. J.; Noest, A. J.; Nibbering, N. M. M. *Int. J. Mass Spectrom. Ion Phys.* 1979, 30, 189.

(51) Di Domenico, A.; Franklin, J. L. *Int. J. Mass Spectrom. Ion Phys.* 1972, 9, 171-184.

of OCC^- with a small concentration of HNO_3 impurity in the NO_2 flow. Formation of neutral products plus an electron (reaction 15a) may arise when the anion attacks the oxygen in NO_2 . The CNO^- (or NCO^-) and CN^- products (reactions 15b and 15c, respectively) may arise from attack on the nitrogen, possibly involving a four-center transition state, while the charge transfer channel (reaction 15d) need not involve an intermediate. The small fraction of charge transfer observed in this reaction despite its exothermicity^{1,54} suggests that charge transfer occurs at close range and must compete with the other efficient reaction channels.

The reactivity of N_2O with carbanions has been characterized and indicates that carbanions with no α hydrogens typically react by oxygen atom abstraction or adduct formation, if at all.⁵⁵ No reaction of OCC^- with N_2O was observed. It is likely that the weak basicity of OCC^- prevents reaction as Bierbaum et al.⁵⁶ have noted that carbanion reactivity with nitrous oxide typically decreases with anion basicity. Similarly, no reaction was observed between OCC^- and N_2 . If reaction of OCC^- with either N_2O or N_2 formed CN_2^- , the reaction would not be observed because the product ion has the same mass as OCC^- . To test for this possibility we made rate coefficient measurements for the reaction of OCC^- with O_2 , where the O_2 was added downstream of a large flow of N_2O or N_2 . No curvature was observed in these semilogarithmic plots, indicating that CN_2^- is not a major product ion.

Reaction of OCC^- with SO_2 results in a product ion of m/e 60. A m/e 80 product arises from a rapid secondary reaction. While signal-to-noise constraints did not allow us to identify the m/e 60 product through observation or absence of the ^{34}S isotope, mechanistic considerations suggest that the reaction forms $\text{OCS}^- + \text{CO}_2$ as opposed to $\text{CO}_3^- + \text{CS}$. The m/e 80 secondary product is then likely to be S_2O^- with an accompanying neutral product of CO_2 . A mass peak at m/e 82 was observed ($^{34}\text{S}^{32}\text{SO}^-$), but the m/e 84 peak ($^{34}\text{S}^{34}\text{SO}^-$), if present, was within the noise level. On the basis of mass alone, the secondary product ion could also be SO_3^- , but formation of this ion from $\text{OCS}^- + \text{SO}_2$ is not energetically accessible. Noting that CO_3^- is known to react with SO_2 to form SO_3^- , completely consistent with our mass peaks, we unsuccessfully attempted to form OCS^- in our source chamber to determine in separate experiments the products of the reaction of OCS^- with SO_2 .

Acidity and Related Thermochemical Data. We have used the bracketing method to determine the acidity of HCCO . The reagents used and results obtained can be found in Table II. In this method, observation of efficient proton abstraction from the neutral reactant to OCC^- indicates that proton abstraction is exothermic and that HCCO is a weaker acid than the neutral reactant, while the absence of proton abstraction suggests that the proton abstraction reaction is endothermic and HCCO is a stronger acid. In this method, a positive result (observation of efficient proton abstraction) provides a firm lower limit to the acidity, while a negative result provides a speculative upper limit because the absence of reaction could be due to other constraints. Proton abstraction is observed from H_2S , CF_3CCH , CH_3NO_2 , CHCl_3 , and $\text{CF}_3\text{CH}_2\text{OH}$ but is not very efficient in any of these reactions. A small efficiency can be the result of a reaction being slightly endothermic. However, it is likely that proton abstraction is exothermic in the reaction with H_2S because proton abstraction is observed from several other compounds which are less acidic than H_2S by more than 20 kJ mol⁻¹. No proton abstraction was

(52) Ervin, K. M.; Ho, J.; Lineberger, W. C. *J. Phys. Chem.* 1988, 92, 5405.

(53) Tsuda, S.; Yokohata, A.; Kawai, M. *Bull. Chem. Soc. Jpn.* 1969, 42, 1515.

(54) Li, W.-K.; Baker, J.; Radom, L. *Aust. J. Chem.* 1986, 39, 913-921.

(55) Kass, S. R.; Filley, J.; Van Doren, J. M.; DePuy, C. H. *J. Am. Chem. Soc.* 1986, 108, 2849.

(56) Bierbaum, V. M.; DePuy, C. H.; Shapiro, R. H. *J. Am. Chem. Soc.* 1977, 99, 5800.

Table II. Bracketing Reactions of OCC⁻ Used in Acidity Evaluation

neutral reactant (HA)	$\Delta H^\circ_{\text{acid}}(\text{HA})$	$\Delta G^\circ_{\text{acid}}(\text{HA})$	proton abstraction?	reaction? ^a
H ₂ S	1469 ± 9	1443 ± 8	yes	yes
CF ₃ CCH	1486 ± 9	1454 ± 8	yes	yes
CH ₃ NO ₂	1491 ± 12	1463 ± 8	yes	yes
CHCl ₃	1494 ± 26	1461 ± 25	yes	yes
CF ₃ CH ₂ OH	1514 ± 15	1482 ± 8	yes	yes
CH ₃ CHO	1531 ± 12	1502 ± 8	no	yes
CH ₃ C(O)CH ₃	1544 ± 11	1514 ± 8	no	yes
HF	1554 ± 1	1530 ± 2	no	no ^b
CH ₂ Cl ₂	1567 ± 16	1535 ± 13	no	yes
HCCO	1576 ± 10	1542 ± 8	no	no ^b
CH ₃ CH ₂ OH	1579 ± 10	1551 ± 8	no	yes
C ₇ H ₈ (toluene)	1593 ± 10	1564 ± 10	no	no ^c
CH ₃ CCH	1592 ± 11	1556 ± 13	no	no

^a "Yes" indicates that reaction of any type was observed between OCC⁻ and the reactant neutral, as indicated by a measurable rate coefficient.

^b Loss in overall ion signal was observed but is suspected to arise from impurities in the neutral reagent sample/flow. Reaction of the indicated neutral with C₂O⁻ is at most slow, as indicated by the rate coefficient limit given in Table I. ^c See Table I.

observed in the reaction with HF. Since no other competing channels are observed and efficient proton abstraction has been observed from HF in other reactions (see, for example, Ervin et al.⁵⁷), we presume that no reaction is observed because it is endoergic. Using these observations we set firm brackets for $\Delta G^\circ_{\text{acid}}$ of $1502 \pm 8 > \Delta G^\circ_{\text{acid}}(\text{HCCO}) \geq 1443 \pm 8 \text{ kJ mol}^{-1}$ and for $\Delta H^\circ_{\text{acid}}$ of $1554 \pm 1 > \Delta H^\circ_{\text{acid}}(\text{HCCO}) \geq 1469 \pm 9 \text{ kJ mol}^{-1}$. These limits on $\Delta H^\circ_{\text{acid}}(\text{HCCO})$ neglect the relatively small difference in entropic terms between HCCO and the reference acid. The $\Delta H^\circ_{\text{acid}}(\text{HCCO})$ limits are given in boldface in the fifth and sixth columns of Table III. A less conservative bracket, using the observation of proton abstraction from CH₃NO₂ and lack of proton abstraction in reaction with CH₃CHO, gives $1502 \pm 8 > \Delta G^\circ_{\text{acid}}(\text{HCCO}) \geq 1463 \pm 8 \text{ kJ mol}^{-1}$ and $1531 \pm 12 > \Delta H^\circ_{\text{acid}}(\text{HCCO}) \geq 1491 \pm 12$, neglecting differences in $\Delta S^\circ_{\text{acid}}$ between HCCO and the reference acids. (Using the reaction with CHCl₃ for the lower limit results in approximately the same bracketing values but with larger error bars due to the large uncertainty in the value of its acidity).

We can use these experimental acidity values to bracket the hydrogen bond dissociation energy in HCCO from the thermochemical equation

$$\Delta H^\circ_{298}(\text{H}-\text{CCO}) = \Delta H^\circ_{\text{acid}}(\text{HCCO}) + \text{EA}(\text{OCC}) - \text{IP}(\text{H}) \quad (16)$$

where we ignore the difference in integrated heat capacities of OCC and OCC⁻ between 0 and 298 K and note that $\text{IP}_{298}(\text{H}) = \text{IP}_0(\text{H})$. The possible error in the bond dissociation energy with this assumption is likely to be $\sim 3 \text{ kJ mol}^{-1}$. Using the electron affinity of OCC determined by Oakes et al.¹ of $1.848 \pm 0.027 \text{ eV}$ and the ionization potential of the hydrogen atom³ of $1312.02 \text{ kJ mol}^{-1}$, we find that $397 \pm 12 > \Delta H^\circ_{298}(\text{H}-\text{CCO}) \geq 357 \pm 12 \text{ kJ mol}^{-1}$.

The bond dissociation energy can then be used to bracket the heat of formation of OCC from

$$\Delta H^\circ_f(\text{OCC}) = \Delta H^\circ_{298}(\text{H}-\text{CCO}) + \Delta H^\circ_f(\text{HCCO}) - \Delta H^\circ_f(\text{H}) \quad (17)$$

where we use the established literature value² for $\Delta H^\circ_{f298}(\text{H})$ and the value for $\Delta H^\circ_f(\text{HCCO})$ derived from the work of Oakes et al.¹ (which ignores the difference in integrated heat capacities between HCCO and HCCO⁻ between 0 and 298 K). Our data bracket this value for $\Delta H^\circ_f(\text{OCC})$ between 316 ± 15 and $356 \pm 15 \text{ kJ mol}^{-1}$. This enthalpy can be combined with the electron

affinity¹ of OCC and the integrated heat capacity of the electron between 0 and 298 K to yield a value for the heat of formation of OCC⁻ as

$$\Delta H^\circ_f(\text{OCC}^-) = \Delta H^\circ_f(\text{OCC}) - \text{EA}(\text{OCC}) - \frac{5}{2}(RT) \quad (18)$$

Equation 18 uses the "thermal electron" convention (described by Henschman⁵⁸ and Lias et al.³ and used in the JANAF Thermochemical Tables²). We find that $172 \pm 15 > \Delta H^\circ_f(\text{OCC}^-) \geq 131 \pm 15 \text{ kJ mol}^{-1}$. These limits on $\Delta H^\circ_f(\text{OCC}^-)$ can be compared with the lower bound of $\geq 148 \pm 12 \text{ kJ mol}^{-1}$ set by the observation of H atom abstraction from CH₂Cl₂ to OCC⁻ in reaction 7c.

Finally, we can use the anion heat of formation and known fragment heats of formation² to bracket the C-CO, C₂-O, and C₂-O⁻ bond energies. We find that $\Delta H^\circ_{298}(\text{C}-\text{CO})$ is between 312 ± 15 and $352 \pm 15 \text{ kJ mol}^{-1}$, $\Delta H^\circ_{298}(\text{C}_2-\text{O})$ is between 601 ± 18 and $642 \pm 18 \text{ kJ mol}^{-1}$, and $\Delta H^\circ_{298}(\text{C}_2-\text{O}^-)$ is between 777 ± 18 and $818 \pm 18 \text{ kJ mol}^{-1}$. The C-CO bond is the weakest bond in the ion by approximately 300 kJ mol^{-1} . As suggested at the outset and demonstrated by the chemistry observed, this fact contributes to the propensity of OCC⁻ to break the C-CO bond in chemical reactions and often transfer a C⁻ to the neutral reaction partner. Loss of O or O⁻ from the anion is energetically much more expensive and does not occur.

The bracketing experiments presented here are the first direct probe of the acidity of HCCO. Related measurements in this work and in the literature can be used to calculate the acidity as well. We summarize in Table III the acidity and related thermochemical values derived from this work and those derived from the literature. The value for the thermochemical parameter which is most closely associated with the original work appears in boldface type. Estimated error for each value is described by the adjacent parenthetical value. The observation of H atom transfer in reaction 7 places a limit on $\Delta H^\circ_f(\text{OCC}^-)$ of $\geq 148 \pm 12 \text{ kJ mol}^{-1}$. This limit is reported in boldface type in the last column of Table III. This limit assumes a value of $108 \pm 4 \text{ kJ mol}^{-1}$ for the heat of formation of CHCl₂ which is the value selected in the Physical and Chemical Reference Data tables.³ Somewhat lower values for $\Delta H^\circ_f(\text{CHCl}_2)$ have been reported by Holmes and Lossing⁵⁹ and Andrews et al.⁶⁰ By rearranging eqs 16-18 and utilizing this limiting value of $\Delta H^\circ_f(\text{OCC}^-)$ we calculated associated thermochemical parameters. These derived values are listed in the last column in standard type face. Several experimental studies have led to determinations or limits on the heat of formation of OCC, two of which are listed in Table III. The value for $\Delta H^\circ_f(\text{CCO})$ attributed to Palmer and Cross⁶¹ is the value given in the JANAF Thermochemical Tables² and was calculated from their experimental value for the equilibrium constant for the decomposition of carbon suboxide into OCC + CO and established values for the heats of formation of C₃O₂ and CO. This $\Delta H^\circ_f(\text{CCO})$ value is given in boldface type in the second column of Table III. By rearranging eqs 16-18 and utilizing this value of $\Delta H^\circ_f(\text{CCO})$ we calculated related thermochemical parameters which are listed in the same column. The smaller upper limit on $\Delta H^\circ_f(\text{CCO})$ provided by Laufer,⁶² given in boldface type in column 3 of Table III, is calculated from the measured photodissociation threshold of ketene-d₂ to form OCC + D₂ and the established heats of formation of ketene and D₂. This value assumes the heat of formation of deuterated ketene is the same as that of ketene, which is likely to lead to an error of $< 1 \text{ kJ mol}^{-1}$. All other values in the column are derived from this $\Delta H^\circ_f(\text{CCO})$ value and rearrangements of eqs 16-18. Finally,

(58) Henschman, M. In *Symposium on Atomic and Surface Physics*, '90; Märk, T. D., Howorka, F., Eds.; Studia Studienförderungsgesellschaft m.V.H.: Innsbruck, 1990; p 217.

(59) Holmes, J. L.; Lossing, F. P. *J. Am. Chem. Soc.* **1988**, *110*, 7343.

(60) Andrews, L.; Dyke, J. M.; Jonathan, N.; Keddar, N.; Morris, A.; Ridha, A. *J. Phys. Chem.* **1984**, *88*, 2364.

(61) Palmer, H. D.; Cross, W. D. *Carbon* **1966**, *3*, 475.

(62) Laufer, A. H. *J. Phys. Chem.* **1969**, *73*, 959.

(57) Ervin, K. M.; Gronert, S.; Barlow, S. E.; Gilles, M. K.; Harrison, A. G.; Bierbaum, V. M.; DePuy, C. H.; Lineberger, W. C.; Ellison, G. B. *J. Am. Chem. Soc.* **1990**, *112*, 5750-5759.

Table III. Related 298 K Thermochemical Values, Measured and Calculated (kJ mol⁻¹)^a

parameter	Palmer & Cross ^b	Laufer et al. ^c	Bauschlicher & Langhoff ^d	this work		
				proton abstraction ^e		H abstraction ^f
$\Delta H^\circ_{\text{acid}}(\text{HCCO})$	1461(64)	$\leq 1509(9)$	1538(9)	<1531(12)	$\geq 1491(12)$	$\geq 1507(15)$
$\Delta H^\circ(\text{H}-\text{CCO})^\#$	327(64)	$\leq 375(9)$	404.6(8.4)	<397(12)	$\geq 357(12)$	$\geq 373(15)$
$\Delta H^\circ_f(\text{CCO})$	286.6(63)	$\leq 334.5(1.7)$	364(12)	<356(15)	$\geq 316(15)$	$\geq 332(12)$
$\Delta H^\circ_f(\text{CCO}^-)$	102(63)	$\leq 150(3)$	179.5(12)	<172(15)	$\geq 131(15)$	$\geq 148(12)$
$\Delta H^\circ(\text{C}-\text{CO})^\#$	382(63)	$\geq 334(3)$	305(12)	>312(15)	$\leq 352(15)$	$\leq 336(12)$
$\Delta H^\circ(\text{C}_2-\text{O})^\#$	671(64)	$\geq 623(11)$	593(16)	>601(18)	$\leq 642(18)$	$\leq 625(16)$
$\Delta H^\circ(\text{C}_2-\text{O}^-)^\#$	847(64)	$\geq 799(11)$	769(16)	>777(18)	$\leq 818(18)$	$\leq 801(16)$

^a The value for the thermochemical parameter which is most closely associated with the original work appears in bold numbers. All other values in each column are calculated by using this value and literature values for the thermochemical quantities relating this value to the identified thermochemical parameter. See text for details. Estimated error for each value is described by the adjacent parenthetical value. ^b Reference 61. ^c Reference 62. ^d Reference 9. ^e Values derived from bracketing experiments. See text for details. ^f Values derived from the appearance of H atom transfer from CH₂Cl₂ to CCO⁻. See text for details. ^g Bond dissociation energy.

in a theoretical investigation, Bauschlicher and Langhoff⁹ calculated the H-CCO bond dissociation energy, given in boldface type in column 4 of Table III. All other values in the column are derived from this bond dissociation energy and rearrangements of eqs 16-18.

While the brackets on the acidity of HCCO provided by our work are consistent with the values derived from the experimental and theoretical work in the literature, none of the related thermochemical data presented are well-defined. Values from Laufer's experiments⁶² and Bauschlicher and Langhoff's calculations⁹ are in disagreement. The limit set by Laufer depends on his assignment of the D₂ observed to the decomposition of ketene-d₂ to OCC + D₂. While similar calculations by Bauschlicher and Langhoff⁹ on the bond dissociation energy of H-HCCO are in excellent agreement with the experimental value derived from measurements of the gas-phase acidity of H₂CCO and the electron affinity of HCCO,¹ their discussion of the H-CCO bond dissociation energy calculation noted a possible bias due to changes in the OCC fragment bonding. Perhaps more important, Bauschlicher and Langhoff's calculation assumed a linear ground state geometry for HCCO, while earlier calculations by Harding⁶³ found a bent ground state geometry. The bent geometry is consistent with the photoelectron spectra of HCCO⁻ reported by Oakes et al.¹ Assuming the bent structure is more stable than the linear structure, a recalculation of the bond energy using this more stable structure would result in a larger bond dissociation energy. This correction increases the disparity between the theoretical values and those derived from Laufer's work. We also note that the bond dissociation energy reported by Bauschlicher and Langhoff is the 0 K value and should be corrected to 298 K. Correction to 298 K takes into account the translational and rotational degrees of freedom of the reactants and products. (There is no change in vibrational population due to the large vibrational frequencies.) This correction results in a small increase in the H-CCO bond dissociation energy of 1.5RT (linear HCCO) or RT (bent HCCO). The consequent small correction to the calculated acidity of HCCO is also an increase. In comparison of all the related thermochemical values, it must be kept in mind that other thermochemical values, e.g., $\Delta H^\circ_f(\text{HCCO})$, EA(OCC), $\Delta H^\circ_f(\text{CH}_2\text{Cl}_2)$, and $\Delta H^\circ_f(\text{CHCl}_2)$, are used and could be a source of error. For example, the electron affinity of OCC could be in error if the origin of the photoelectron spectrum were not chosen correctly, a possibility that the authors¹ noted. Clearly, more work is needed to define better these important thermochemical parameters.

Conclusions

The radical anion OCC⁻ is a versatile anion, participating in nucleophilic displacement, C⁻ and electron transfer, H, H⁺, and

H₂⁺ abstraction, and reactive electron detachment reactions. Many of the reactions explored in this work indicate that OCC⁻ has a propensity to react by attack of the terminal carbon on the reactant neutral followed by cleavage of the C-CO bond. As a result, reactions are observed which apparently form CO or CO₂ as the product neutral. This characteristic reactivity is completely consistent with the ²Π ground state electronic configuration for OCC⁻ proposed by Oakes et al.¹

Similarities are observed between the reactions of OCC⁻ and those of O⁻, most notable of which is the H₂⁺ abstraction reaction which has been exploited by others to form novel carbene anions.²⁶ The weaker basicity of OCC⁻ as compared with O⁻ suggests that novel anions may be formed from reaction with OCC⁻ when it is inefficient or not possible to form the anion in reaction with O⁻ because of competing proton abstraction. However, the range of species with which OCC⁻ may abstract an H₂⁺ will be restricted as compared with that of O⁻ because forming ketene from OCC⁻ has a smaller energetic driving force than does forming water from O⁻.

Reactive electron detachment occurs in many reactions and is the dominant product in the reaction of OCC⁻ with several organic species. While reactive electron detachment channels have not commonly been reported in the literature,⁴⁰ this and other recent work shows that such reactions can be a common reaction channel for ion-molecule reactions, especially in reactions of radical anions, and that the efficiency of these channels can range from the most efficient to the very inefficient.^{4,22,38,42-47} Identification of reactive electron detachment channels requires an ability to monitor total ion signal in the absence of species detection discrimination, an ability to measure relative ion signals and evaluate relative detection sensitivities, or an ability to monitor free electrons. A SIFT with the ability to monitor an ion current representative of the flow tube ion density, such as used in these experiments, is well suited for such investigations.

Thermochemical data for OCC⁻ and related species derived from this work provide information important in the chemistry of hydrocarbon oxidations, especially oxidation reactions at high temperatures. However, further work is needed to better define these parameters.

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(63) Harding, L. B. J. Phys. Chem. 1981, 85, 10.

(64) Su, T.; Chesnavich, W. J. J. Chem. Phys. 1982, 76, 5183.

(65) Su, T. J. Chem. Phys. 1988, 89, 5355.